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Heavy Metals Levels in the Water of the Tigris River in the City of Mosul, Iraq

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ABSTRACT

Drinking water sources suffer at the present time from great pollution as a result of population, industrial and agricultural growth and expansion, as well as the lack of proper planning in building cities. Since the Tigris River is the only water resource for the city of Mosul, the current study was conducted to assess the pollution of river water in the city of Mosul via estimating the concentration of some heavy metals (Fe, Co, pb, Zn and Cu) in the river water, passing through the city of Mosul. This work examined the water quality of the Tigris River to maintain its good quality and cleanliness. The sampling sites extend from the Kubba area in the North, where the river enters the city of Mosul to the Yarmajeh area in the South, where the river leaves the city for a period of 6 months, starting from September 2020 to February 2021. The results showed that, the average water temperature ranged between 10 and 20°C. The values of the copper element were imperceptible during the study period, while the zinc element recorded concentrations ranging between 0.443 and 1.163mg/ liter in the river water, and the values of lead and cobalt ranged between 0.222- 3.770 and 0.750- 2.835mg/ liter, respectively; while, the iron element in the river water showed values ranging between 0.502 and 1.714mg/ liter. The results indicate that the heavy elements (lead, cobalt and iron) exceeded the standard parameters allowed by the World Health Organization for the water of the Tigris River passing through the city, and the last location (the Yarmajeh area) was the recorded the most polluted site under study.

INTRODUCTION

The study of water pollution is radical since it is related to the life of living organisms, especially that water is used for drinking and irrigation purposes. Drinking water sources suffer at the present time from great pollution as a result of population growth and expansion, industrial and agricultural, as well as the lack of proper planning in building cities, all of which lead to doubling the quantity of household, industrial and agricultural wastes entering the water body. Thus, it has become necessary to monitor the quality of water and evaluate the work of the liquefaction stations located on it as a result of the continuous qualitative change in the aquatic environment **(Mahmoud, 2015; Mohammad, 2022)**; water pollutants include heavy metals, which are called heavy elements. Any element in water whose density is greater than 5g/ cm^3 is considered toxic even at low concentrations. It is considered one of the dangerous pollutants found in the fresh water environment, which in turn causes an imbalance in the environmental equilibrium that is directly or indirectly reflected on living organisms **(Al-Saadi, 2006;**

Aboud *et al*., 2015; Al-Sarraj *et al.*, 2019).

Heavy metals are found in the aquatic environment in many forms that differ in their toxicity and vital readiness, they may be in the form of suspended particles or in the form of dissolved ions, organic or inorganic complexes **(Tokalioglu *et al.*, 2000)**. Despite the importance of some vital heavy metals, they have a toxic effect due to their stability in the environment and their spreading for long distances from their sources through rain, storms and winds, as well as the inability to decompose by microorganisms and other natural processes **(Gulfraz *et al*., 2001; Feng *et al*., 2008)**. These elements are dangerous to human health since they exist at the top of the food pyramid, serving as the final repository for the accumulation of these elements in the body of the organism. Heavy elements can bioaccumulate in living organisms' bodies, and their concentrations increase through the food chain for they enter through the soil, water and air into the bodies of living organisms, which lead to the occurrence of bioaccumulation (**Aoyoma *et al*., 1978; Ahmed *et al*., 2010**), causing river contamination with high levels of heavy metals.

Moreover, **Abdul-Kareem *et al*. (2011**) studied some heavy metals (iron, zinc, lead nickel and cadmium) in the water of the Tigris River in Baghdad City, as they confirmed that the Tigris River in the study area is contaminated with some heavy metals, especially lead and cadmium. The previous authors found that, the concentration of iron was between 0.01 &1.06mg/ l; zinc was between 0.1 & 0.4mg/ l, and the range of lead was between 0.01 & 0.15mg/ l, and both cadmium and nickel recorded concentrations within the range of 0.01 & 0.05 and 0.01 & 0.04mg/ L, respectively. **Al -Nuaimy and Al-Shama'a (2019)** estimated the heavy metals (iron, copper and lead) in the water of the Khosr River from the source to the downstream in the Tigris River. The results of the study indicated that, the heavy elements values differed according to the location, as the lead values was high in the Khosr. **Al-sarraj and Jankeer (2020)** during their study on the water of the Tigris River reported that, heavy metals polluting the river water in the city of Mosul have a role in inhibiting the activity of the enzyme acetylcholine esterase of two types of fish. While, **Shukri *et al*. (2011)** found that, the pollution of the Tigris River in Baghdad Governorate was related to some heavy metals (zinc and lead), and their results indicated that, no concentrations of zinc or lead were detected in water samples taken from four sites along the river, passing through Baghdad Governorate (Al- Atifiya, Tahrir Bridge, Jadiriyah Bridge, Al-Masbah area). The study of **Abdul-Jabbar *et al*. (2013)** is one of the studies conducted on the Tigris River north Tikrit City to estimate some heavy metals in the river water. The results of the study reported that, the river water was contaminated with heavy metals, including copper, chromium, zinc, nickel, cobalt and cadmium, and the lead element recorded the highest values. In addition, the study of **Al Rudainy (2017)** on the Tigris River estimated the concentration of lead and cadmium in water and specific organs of the Qattan fish off the Tigris River, south of Baghdad Governorate. It was reported that, the average concentration of lead was more than the concentration of cadmium in both water and fish.

Abed and Ahmed (2019) conducted a study to investigate the surface water quality of the Tigris River in the Baiji area in Salah al-Din Governorate and noticed that, the river water in the study area is suitable for drinking purposes in terms of pollution with heavy elements. The aim of the current study was to estimate the pollution of the Tigris River water passing through the city of Mosul with some heavy elements by measuring the concentrations of some elements (iron, cobalt, lead, zinc, copper) in the river water and comparing them with the internationally permitted standards and determinants and determining their quality, considering the river, the main water source on which the city relies.

MATERIALS AND METHODS

Samples were collected from five sites along the course of the river inside the city, starting from the site of the Kubba area (where the river enters the city) in the Rashidiya area; the site of the third bridge; the site of the Freedom Bridge, and the site of the Yarmajeh area where the river exits the city, as shown in Table (1) and Fig. (1). A 6 month- study was conducted from September 2020 to February 2021. Water temperature was measured using a graduated mercury thermometer (0- 100°C). The concentrations of the heavy metals under study (copper, zinc, lead, cobalt, iron) were estimated based on the method mentioned in **APHA (1985)**, as samples were prepared for measurement after being digested using concentrated nitric acid, and the absorbance of the samples was measured Using an atomic absorption spectrometer model (NOVAA 350). Results were expressed in units (mg/L). Statistically, the data were analyzed according to the international trial system and by designing randomized complete sectors with three replicates. Furthemore, Duncan's multiple-range test was used to compare the averages; different treatments were significantly distinguished by different alphabets **(Antar & Al-Wakaa, 2017)**.

Table 1. Sample collection sites along the Tigris River in Mosul City, with their coordinates (From Google Earth)

T	Site	coordinate
1	Kubba	43° 4 ' 57.41069E 36°23' 50.22085N
2	Rashidiya	43°6'23.83624N 36°23'42.83624N
3	The third bridge	43°6'48.89779E 36°21'45.65578N
4	Freedom Bridge	43°8'40.88728E 36°20'22.49898N
5	Yarmajeh	43°9'41.24549E 36°19'29.94304N

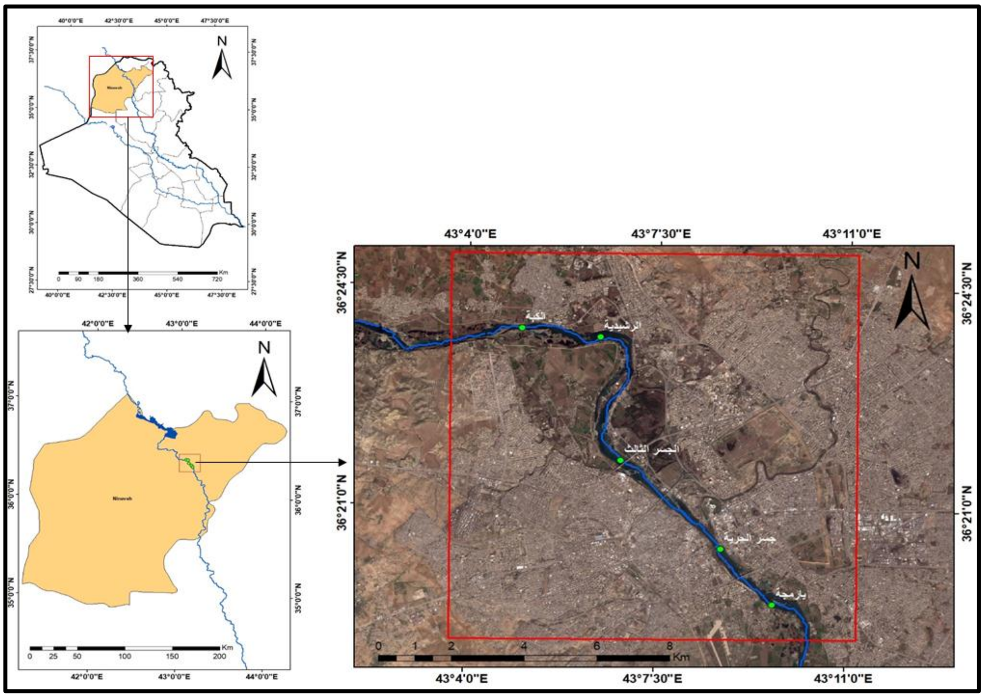

Fig. 1. A map showing the sites under study (From Google Earth)

The Canadian Council of Ministers of the Environment (CCME) initiated the CCME WAI Method which is widely used and globally accepted for assessing water quality.

The CCME WQI model consists of three factors:

1. Scope: representing the number of variables that do not meet their objectives;

2. Frequency: representing the number of times these objectives are not met, and

3. Amplitude: representing the amount by which the objectives are not met.

These factors give a numerical value ranging from 0- 100, referring to the total water quality for the water body, where 0 represents the "worst" and 100 represents the "best". The formulation of the WQI as described in the Canadian Water Quality Index 1.0 was used as follows:

– Technical report was formed via the following equations:

$$F\,1 = \left(\frac{number\ of\ failed\ variables}{total\ number\ of\ variables}\right) x100$$

Where,

F1 is the measure for scope, representing the number of variables whose

value does not match the objectives throughout the study period.

$$F2 = \left(\frac{\text{number of failed tests}}{\text{total number of tests}}\right) x100$$

Where, F2 is the measure for frequency, representing the failed tests which are the percentage of individual tests that do not meet the objectives.

While, F3 stands for the measure for amplitude, representing the number of failed test values that do not meet their objectives. This step consists of several phases. Initially, the calculation of excursion, which represents the number of times by which the test value is greater than the objective; the excursion is calculated using the following equation:

$$\text{Excursion} = \left(\frac{\text{failed test value}}{\text{guide line value}}\right) x\ 100$$

For the cases in which the test value is less than the objective, the succeeding formula is used:

$$\text{excursion} = \left(\frac{\text{guideline value}}{\text{failed test value}}\right) - 1$$

The normalized sum of excursions (Nse) can be calculated via the following equation:

$$N\text{se} = \frac{\sum_{i=1}^{n} Excursion}{\text{number of tests}}$$

Finally, the amplitude (F3) can be determined using the following equation:

$$F3 = \frac{\text{nse}}{0.01\ \text{nse} + 0.01}$$

Then, the CCME WQI is calculated as shown in the following equation:

$$WQI = 100 - \left(\frac{\sqrt{\text{F1}^2 + \text{F2}^2 + \text{F3}^2}}{1.732}\right)$$

In a step forward, the value of water quality can be ranked by relating it to one of the five categories set out in Table (2).

The main pollution parameters that were considered for surface water quality management in this work included 6 parameters (℃, Cu, Zn, Pb, Co, Fe).

$$\mathbf{F1} = \left(\frac{number\ of\ failed\ variables}{total\ number\ of\ variables}\right) x100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

F2 (Frequency): represents the percentage (number) of individuals who failed the tests to the total number of tests.

$$\mathbf{F2} = \left(\frac{\text{number of failed tests}}{\text{total number of tests}}\right) x100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

F_3 (Amplitude): represents the amounts of exceeded tests and calculated through two steps.

1- **Step One**: The number of times the individual concentrations exceed the standard objective limits is called (Excursion). It is calculated as follows:

$$Excursion = \left(\frac{\text{failed test value}}{\text{guideline value}}\right) - 1 \ldots\ldots\ldots\ldots \quad (3)$$

For the cases in which the exceeded test value is greater than the standard object value, it is calculated by inverting the ratio.

2- **Step Two:** The number of the set of individuals exceeding tests is calculated by adding the individual deviations and dividing it by the total number of tests (exceeded and not exceeded). This variable is called the normalization of excursion and is symbolized by (nse):

$$nse = \frac{\sum_{i=1}^{n}}{\text{number of tests}}$$ ....(4)

3- **Step three:** F_3 (Amplitude) can be calculated according to the following equation:

Table 2. CCME WQI categorization schema **(CCME, 2001)**

Category	WQI	Status
1	5	excellent
2	80–94	good
3	65–79	fair
4	45–64	marginal
5	0–44	poor

RESULTS AND DISCUSSION

Water temperature in the study area

The results showed that the water temperature degrees ranged between 10 and 20°C, as the water temperature during the current study recorded its highest value in September 2020 and the lowest in January 2021, as shown in Fig. (2). This finding agrees with those reported in the case studies of **Al-Wattar (2009)** and **Al-Obaidy (2013)** on the part of the Tigris River in Nineveh Governorate.

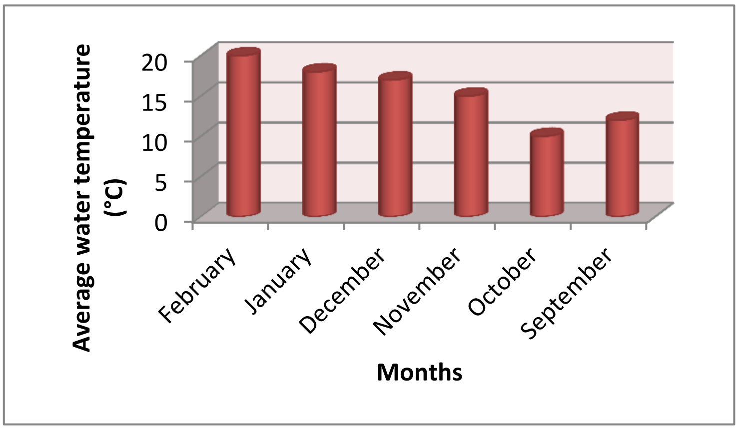

Fig. 2. Average values of water temperature during the study period

Heavy metals in water under study

Recorded imperceptible concentrations in the water of the Tigris River during the study period, and the reason for this may be due to the occurrence of the phenomenon of dilution and diffusion in the river water **(Fares & Shubout, 2015)**. The results of the current study contrast with what **Al-Sarraj (2013)** postulated. The previous author reported that, the concentration of copper in the Tigris River water in the city of Mosul ranged between 0.04 & 0.468mg/ liter and attributed the reason for this to the liquid waste thrown into the river without treatment. In addition, **Abdul-*Jabbar et al.* (2013)** reported that, the concentration of copper ranged between imperceptible & 0.053mg/ liter in the Tigris River water north of the Tikrit city, Salah al-Din Governorate. Copper is important for living organisms for it participates in the formation of many molecules and enzymes including the hemoglobin building pathway, but its presence at concentrations higher than the permissible limits has a toxic effect since it enters the aquatic environment through mines and energy generators **(Said *et al*., 2017)**.

The zinc element (Zu), it recorded concentrations that ranged between (0.443 - 1.163) mg / liter, as shown in Table (3). Reason for the in increase in the concentration of zinc in the river warter may be due to the amount of agricultural domestic and industrial wastes that are thrown in to the river trough estuaries that flow in to it during its flow in to city, as it is noted that the highest concentration was recorded in the last site at Yarmajeh area and the lowest concentration recorded in the second site at Al Rashidiya area, and this was confirmed by the results of the statistical analysis using Duncan's multiple range test, as the zinc component recorded the lowest decrease Significant in the second site (Al Rashidiya) compared to the other sites under study as shown in Table (3). These results are agree with the results of Al-Sarraj study (2013) on the same river section, as it found that the concentration of zinc in the river water ranged between (0.469 - 1.961 mg/ liter), while Shukri *et al.* (2011) found during their study the pollution of the Tigris River in the province of Baghdad with some heavy metals, and no concentration of zinc was found in the river water samples, as the results of the study conducted by Saleh and Saeed (2013) to estimate the concentrations of some heavy metals in the Tigris River water Before and after the filtration plant of Tikrit University, the concentration of zinc in the river water before passing through the filtration plant was (2.3 mg / liter), and its concentration after the river water passed through the filtration plant was (1.3 mg / liter).

Zinc is one of the necessary elements for living organisms at low levels, as it is one of the components of the insulin hormone, and its importance in strengthening the body's immune system, in addition to its importance for the metabolic and reproductive activities of the male and it also helps in fertilization (**Al-Sarraj, 2013; Said *et al*., 2017**).

Table 3: Averages, minimum and maximum limits for the concentrations of the elements under study

Site / metal		(1) Kubba	(2) Rashidiya	(3) third bridge	(4) Freedom Bridge	(5) Yarmajeh	WHO (2017)
Cu mg /L	Meaning	*Nil	Nil	Nil	Nil	Nil	2
	Min	Nil	Nil	Nil	Nil	Nil	
	Max	Nil	Nil	Nil	Nil	Nil	
Zn mg /L	Meaning	0.897	0.78	0.914	0.762	0.833	3
	Min	0.531	0.443	0.627	0.591	0.664	
	Max	1.017	0.889	1.160	0.945	1.163	
Pb mg /L	Meaning	1.785	2.06	1.928	1,939	2.60	0.01
	Min	1.256	1.617	0.962	0.822	1.011	
	Max	2.560	2,621	2.565	3.770	3.696	
Co mg /L	Meaning	0.990	1.039	1.583	1.645	1.72	0.05
	Min	0.750	0.829	0.765	0.809	1.016	
	Max	1.257	1.427	2.835	2.154	2.314	
Fe mg /L	Meaning	0.662	0.677	0.906	0.913	1.144	0.3
	Min	0.502	0.591	0.699	0.750	0.813	
	Max	0.794	0.842	1.566	1.152	1.714	

* Nil = imperceptible concentration

The results of the current study indicated that the concentration of lead in the Tigris River water during the study period ranged between (0.822 - 3.770) mg / liter as shown in Table (3), which exceeded the limits allowed by the World Health Organization (0.01) mg / liter (WHO, 2017). The reason for the increase in the concentration of lead in the river water may be attributed to the direct discharge of untreated wastewater into the river (Al-Yazji and Mahmoud, 2008). The lead element was significantly superior in the other two sites (Al-Hurriya Bridge and Yarmajeh) under study, as shown in Table (3). The results of the current study differed with what Al-Sarraj (2013) found during its study on the Tigris River passing through the city of Mosul. The concentrationn of lead ranged between (Imperceptible - 0.403) mg/L. Shukri *et al.* (2011) also found, during their study of the concentrations of some heavy metals in the Tigris River water passing through the province of Baghdad, that the lead element did not show any significant concentrations in the river water. In a study (**Ahmed, 2013**) to find out the pollution of the Tigris River water with heavy metals in Maysan Governorate, the lead element did not exceed the permissible values for drinking water by the World Health Organization (WHO, 2017). The element lead is one of the most toxic chemical elements and the ability to accumulate in the body of the living organism, as it causes damage to the human nervous system, and the sources of water pollution with lead are many, including sewage and agricultural water and the use of pesticides, and lead is used in modern technology in industries such as mineral extraction and the manufacture of paints. Pesticides and electric batteries, as well as rainwater washes pollutants that eventually move to water bodies (Jankeer, 2012). The results of the current study showed that the concentration of (Co) in The river water ranged between (0.750 - 2.235) mg / liter and it exceeded the limits allowed by the World Health Organization, (0.05) mg / liter (WHO, 2017), during the study period. The reason for the increase in the concentration of cobalt in the river water may be due to the washing and dissolving processes and the amount of dissolved salts in the river water, as well as the processes of weathering rocks in the river basin and the transfer of weathering products to the river water through valleys and seasonal and permanent tributaries, and the effect of the process of feeding the river from groundwater during The rainy season (Thanoun and Mahmoud, 2019). And the cobalt element recorded a significant decrease in the fourth site (the Freedom Bridge), explained in Table (3), and the results of the study contrast with what was indicated by y Abdul-Jabbar and others (2013), when they found during their study of the Tigris River water north of the city of Tikrit that the cobalt element record concentrations ranged between (imperceptible - 0.096) mg / liter. Cobalt is one of the toxic and carcinogenic metal elements, and cobalt is one of the components of tobacco smoke, as the tobacco plant absorbs cobalt from the surrounding soil and concentrates it with other heavy metals in its leaves easily, and these components are later inhaled during tobacco smoking (Cutter and Bruland, 2012).

The results of the current study showed that the concentrations of iron (Fe) river water ranged between (0.502 - 1.714) mg / liter, as it exceeded the limits allowed by the World Health Organization, (0.3) mg / liter (WHO, 2017) during the study period. This may be attributed to the various wastes being dumped into the riverbed inside the city, as well as the type of chemical fertilizers that play an important role in the levels of river pollution (**Farag *et al.*, 2007**). It was also noted the moral superiority of iron in the sites (the third bridge, the Hurriya Bridge and Yarmajeh) under study as shown in Table (4). Through previous studies, we note the fluctuation in the concentration of iron in the river water, as Abdul Kareem and others (2011), that the concentration of iron in the river water passing through the city of Baghdad ranged between (0.01-1.06) mg / liter, and Fares and Shubout (2015) mentioned that the concentration of iron did not register an increase in the Tigris River water in Wasit Governorate and attributed this to the lack of Industrial activity in the region. Iron is one of the useful and necessary mineral elements for the human body, but high levels of it above normal levels lead to serious damage to the body, including liver diseases and various infections. In addition, its deficiency from the normal limit is the most common form of malnutrition in the world (**Muhly, 2003**).
The results of the analysis of variance in Table (5) showed a significant superiority of the elements (Zn, pb, Co, and Fe) in February during the study months, and the (Zn) element recorded the significant decrease in the month of September, while the least significant decrease of (pb) was in September and November, while (Co) element recorded a significant decrease in October and November, iron element showed a significant decrease in November and December during the study period.

Table 4. The locational significant differences between the sites under study

No.	Sites	Zn	Pb	Co	Fe
1	Kubba	0.9570 a	1.8328 b	1.2161 d	0.7483 b
2	Rashidiya	0.7883 b	1.9572 b	1.2817 d	0.7789 b
3	Third Bridge	0.8372 ab	2.0073 b	1.8044 b	0.9678 a
4	bridge Freedom	0.8328 ab	2.0878 ab	1.5483 c	1.0506 a
5	Yarmajeh	0.8472 ab	2.4033 a	2.0856 a	0.9900 a

Table 5. The temporal significant differences of the studied elements during the months of the study

Months	Zn	Pb	Co	Fe
September	0.6193 b	1.4980 c	1.1320 d	0.7180 d
October	0.8951 a	1.9347 b	1.1900 cd	0.7120 d
November	0.9873 a	1.3768 c	1.3587 c	0.7920 cd
December	0.8500 a	2.4140 a	1.6720 b	0.8893 c
January	0.8460 a	2.5333 a	2.1513 a	1.0280 b
February	0.9173 a	2.5893 a	2.0193 a	1.3033 a

The differences were calculated at the 0.05 level of significance, the averages with similar letters do not differ significantly, and the means with different letters differ significantly at the 0.05 level of significance according to Duncan's multi-range test.

The results of the water quality index indicated that the river water quality is poor in the sites under study during the study period based on the concentrations of the studied elements, as the index values ranged between (15.95-16.02), Fig. (5).

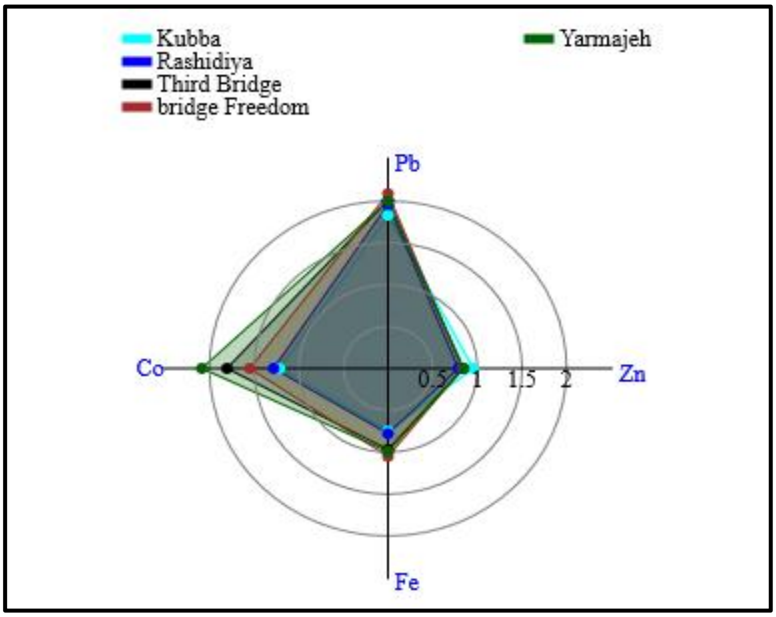

Fig. 3. Radar chart show the mean concentration of heavy metals in studied sites

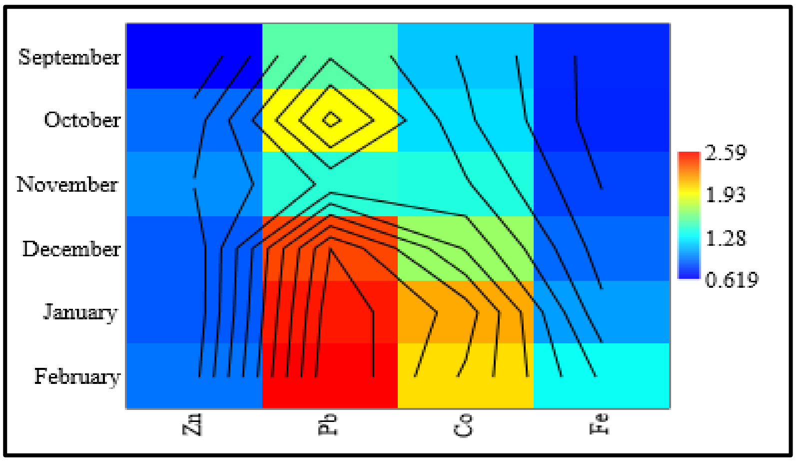

Fig. 4. Radar chart show the mean concentration of heavy metals in studied sites

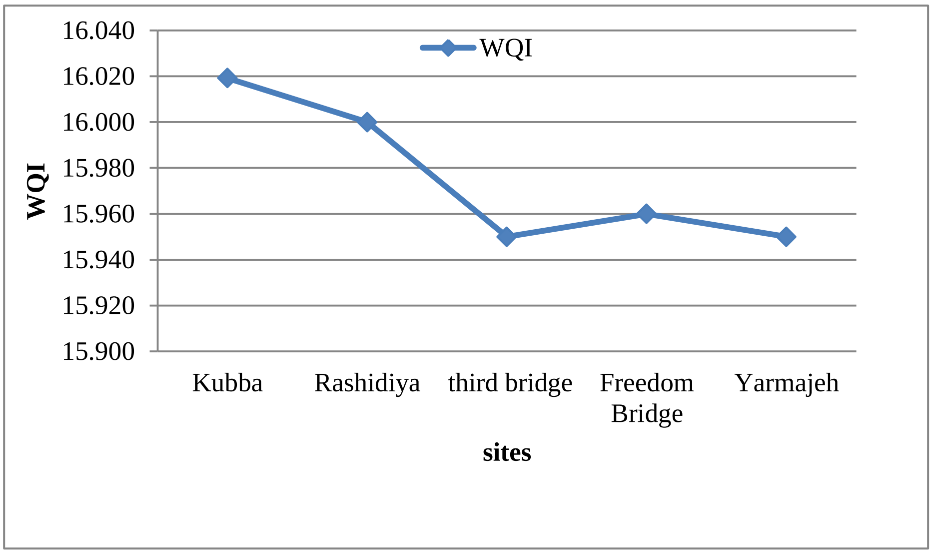

Fig. 5. Water quality index values of different sites by using CCME WQI model

CONCLUSION

Through the results of analyzes of heavy metals in the Tigris River water passing through the city of Mosul, and after comparing them with local and international standards and determinants, we found that the concentrations of elements (lead, cobalt and iron) exceeded the permissible standard determinants. The analyzes of copper in the river water within the area under study showed imperceptible concentrations throughout the study period.

The results of the study showed that the concentrations of the elements under study showed a remarkable increase in the river water when it passed through the city of Mosul, as the last site (Yarmajeh area) was the most polluted site under study.

Finally the Tigris river water can't be used for drinking directly. However a per-treatment is needed before the drinking use.

RECOMMENDATIONS

Conducting a study to treat the waste water before it is put into the river water. Spreading environmental awareness among the owners of factories and commercial activities and urging them to take care of treating the waste before putting it into the river. Conduct studies that include other chemical elements and estimate their concentrations in river water. And conducting diagnostic studies for the types of phytoplankton present and using them as vital evidence of river pollution.

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